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Energy transfer in oligothiophene inclusion compounds

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Abstract

Energy transfer between terthiophene and quinquethiophene oligomers embedded in the nanochannels of perhydrotriphenylene crystals is investigated by fs-time-resolved photoluminescence spectroscopy. Excitonic effects in these compounds are suppressed due to the large intermolecular distances imposed by the host crystal. Very efficient transfers of the electronic excitations from donor (terthiophene) to acceptor (quinquethiophene) molecules are observed. A quantitative analysis of the experimental data show that energy migration mainly occurs via direct donor-acceptor single-step transfer.

Keywords: Energy transfer, Inclusion compounds, Oligothiophenes, Time-resolved spectroscopy.

1. Introduction

Molecular systems incorporated along channels of host materials like zeolites or perhydrotriphenylene (PHTP) are attracting a considerable interest for their potential applications [1]. The processes of energy transfer among the incorporated guest molecules are a central issue of the photophysics of these systems.

In this work, we present a study of the excitation energy transfer between two oligothiophenes of different lengths, namely the quinquethiophene (T5) and terthiophene (T3), which are accommodated in the nanochannels of a PHTP host crystal.

2. Experimental

Oligothiophenes inclusion compounds (Tn-IC) are obtained by melting and successively cooling the molecules with perhydrotriphenylene in excess respect to the stoichiometric value as described elsewhere [2]. Co-inclusion of T5:T3 mixtures were obtained by the same procedure with different molar ratios.

The emission was excited by the second harmonic of a mode locked Ti:Sapphire with typical pulse width of 100 fs tuned at 810 nm. The PL signal was temporally analyzed by using nonlinear optical gates technique allowing for a time resolution of 200 fs, and a Hamamatsu optical sampling oscilloscope with 20 ps time resolution.

3. Results and Discussion

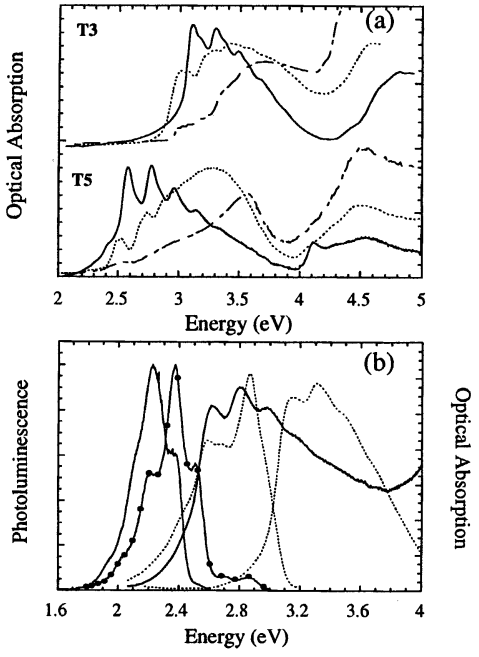

Fig. 1. (a) Optical absorption of T3 and T5 powders (dotted lines), evaporated films (dashed lines) and inclusion compounds (solid lines) at 80K. (b) Photoluminescence and absorption spectra of T3 (dotted line) and T5 (solid line) inclusion compounds. Photoluminescence of the inclusion compound T5:T3 = 0.006 (full circles). T = 300 K.

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In Fig 1(a) the optical absorption spectra of T3 and T5 are shown for the powders, evaporated films, and inclusion compounds. The strong spectral variations observed in aggregated molecules with respect to the weakly interacting Tn-IC molecules are consistent with the fact that intermolecular interactions spread the excited state molecular levels into an exciton band [3]. Differently from aggregated molecules, in the inclusion compounds, thiophene molecules display optical absorptions very similar to those of frozen solutions indicating that excited state interactions are suppressed due to the large distances d=14Å between molecules in the PHTP channels.

The spectral overlap between the emission spectrum of the donor and the absorption spectrum of the acceptor is an important prerequisite to get an efficient intermolecular energy transfer via dipole-dipole coupling [4]. This condition is very well satisfied, as shown in Fig. 1(b), by T3 and T5.

The PL spectrum of the co-inclusion compounds with molar ratio T5:T3=x as low as 0.006 is reported in Fig. 1b. In spite of the very low T5 concentration, excitation within the T3 absorption gives rise to a dominant T5 emission. This result demonstrates that efficient energy transfer processes take place among molecules. It is important to stress that the relative intensity of the T5 and T3 emissions does not depend on temperature.

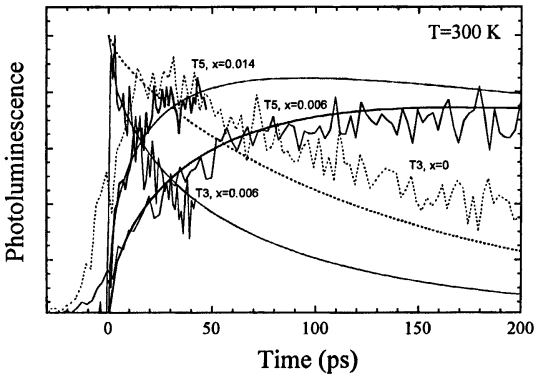

Fig. 2. Photoluminescence transients of the T3-IC (scattered dotted line), of T5 for T5:T3 = x = 0.006, of T5 for x = 0.014 and of T3 for x = 0.006 (scattered solid line). Numerical simulations following the model described in the text are reported as solid smooth curves. The smooth dotted line is the emission decay of T3 for x = 0.006 following the analytical solution of the Förster model [4] as explained in the text. PL data extending up to 200 ps have been recorded using a streak camera.

In Fig. 2, we show the time resolved PL emissions for the T3-IC and for the co-inclusion compound with x=0.014 and 0.006. The rise time of theT5 emission and the decay time of the T3 emission become longer for decreasing concentration. These results provide a further and complementary confirmation of the efficient T3→T5 energy transfer. The presence of an acceptor molecule at the site *i* of the PHTP crystal gives rise to a deactivation pathway for the excited T3 molecules. According to Förster's theory and neglecting T3→T3 energy migration, the T3→T5 transfer rate $1/\tau_{da}$ is equal to $\Sigma_i(\chi_i^2/\tau_d)(R_0/R_i)^6$, where R_0 is the Förster's radius, R_i is the donor to acceptor distance, τ_d is the natural decay time of T3-IC, χ_i is a factor depending on the relative orientation of the T3 and T5 dipoles, and the summation extends over all the crystal sites occupied by an acceptor molecule. The rate equations describing the fractions of T3 and T5 in the excited state are $dn_d/dt=-n_d/\tau_d - n_d/\tau_{da}$ and $dn_a/dt=-n_a/\tau_a + n_d/\tau_{da}$, respectively. Once $1/\tau_{da}$ is known for a given configuration (k) of acceptor and donor molecules in the host crystal, the solutions of the previous equations are $n_d(k) \propto exp[-t/\tau(\kappa)]$ and $n_a(k) \propto exp[-t/\tau_a]-exp[-t/\tau(k)]$, with $1/\tau(k) = 1/\tau_d + 1/\tau_{da}(k)$. The radiative emission rates from donors and acceptors are proportional to the average of the previous quantities, i.e., $<n_d>=\Sigma_k n_d(k)w(k)$, and $<n_a(k)>=\Sigma_k n_a(k)w(k)$, respectively, where $w(k)$ is probability that the configuration (k) occurs for a given concentration.

For a fixed x, we have simulated the temporal behavior of the acceptor and donor PL by calculating $<n_d>$ and $<n_a>$ in PHTP nanocrystals containing up to *216000* molecules, and making the average over up to *1000* different random configurations (k). We have assumed that oligothiophenes completely fill the PHTP nanochannels with intrachannel and interchannel distances between molecule barycentres of *1.6* and *1.3 nm*, respectively [2]. The calculated PL temporal dynamics are shown in Fig.2. The agreement with the experimental results is excellent. Since all the inputs of the model (R_0=*4.9 nm*, τ_d=*170 ps*, τ_a=*880 ps*) are experimentally available [5], no fitting parameters are used in the numerical simulations. For comparison, the T3 decay for x=*0.006* is calculated following the analytical expression $<n_d> \propto exp[-t/\tau_d - 2\beta\tau^{0.5}]$ (2β = *0.021* $ps^{-0.5}$) given in Ref. [4], obtained assuming a continuous distribution of point-like molecules. This expression, used to fit experimental data in guest-host polymer systems [6], strongly understimates the T3→T5 transfer rate.

In conclusion, we have investigated the energy transfer from terthiophene to quinquethiophene molecules embedded in nanochannels of perhydrotriphenylene. Single-step Förster energy transfer provide an excellent quantitative description of the decay and build up, respectively, of the donor and acceptor populations as determined by time-resolved photoluminescence experiments.

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